

The link between function and structure of esters

■ Felix Wilson, Dani Loughran - Aston Chemicals, UK

Esters are one of the most widely used types of chemical compound in the world today. Their simple but versatile chemistry is used in applications as diverse as plastics, resins, explosives, bio-fuel, lubricants, paper, and in cosmetics and the personal care industry.

The majority of esters are either derived synthetically from petroleum or from natural triglycerides. The basic synthesis is shown in Figure 1. Petroleum-derived esters are expected to become more expensive due to the extreme variability of crude oil prices, which is likely to reduce their use.^{1,2}

Growth in the global ester market is expected to be primarily driven by the increasing demand for esters in the biofuel and cosmetic industries. There is also an increasing demand for natural alternatives to petroleum-derivatives in personal care,¹ which could be met by increased use of naturally derived esters.

Structure relating to function

In the cosmetics industry, the versatility of esters is demonstrated by their use in an extremely wide variety of applications. Short-chain esters are the volatile molecules that give many fruits, including pineapple, strawberries and apples, their distinctive aromas.^{3,4} For this reason short chain esters such as Benzyl Acetate are predominantly used in fragrances. Long-chain esters, with over 30 carbons, can be used to structure sticks or to thicken and stabilise emulsions in cosmetics, with a common example

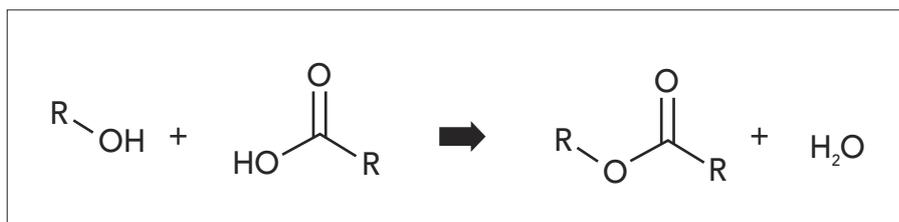


Figure 1: A reaction scheme for ester synthesis from an alcohol and a carboxylic acid.

being the wax ester, Cetyl Palmitate.

This article will be focused on esters with medium sized chain lengths, with 15 to 30 carbons. These are used as emollients in the cosmetic industry and have a large number of properties that are highly beneficial in the personal care market. Esters provide a drier feel than traditional oils, reducing the greasy feel of formulations. They excel in the solubilisation of organic UV filters and in pigment wetting. These properties enable esters to be highly beneficial to sun care and colour cosmetics, as well as improving the sensory properties of skin care formulations.

As previously discussed, one of the main reasons for the growth in the ester market is the potential to create esters using natural raw materials. With natural cosmetics becoming ever more important, having truly functional natural alternatives to synthetic ingredients is crucial.

Esters can provide formulators with effective and natural replacements for potentially unwanted materials such as mineral oils and silicones.

Sensorial properties of ester emollients

The performance of emollients such as esters can have a huge effect on the final formulation. With hundreds of emollients to choose from, it can be difficult to know which materials will give a suitable skin-feel to the formulation without testing each one. This would clearly be time consuming and inefficient. With some understanding of the underlying chemistry of each material however, an estimation of relative skin-feel can be made.

The feel of an ester is dependent on its chemical structure, and understanding how this impacts the sensory properties of the ester can help formulators to choose the most appropriate material for each formulation.

London dispersion forces

The skin-feel of an emollient and in particular the feel upon application is due to electrostatic intermolecular forces. The primary intermolecular forces of interest in this case are London dispersion forces, which form the dispersion contribution of van der Waals forces.

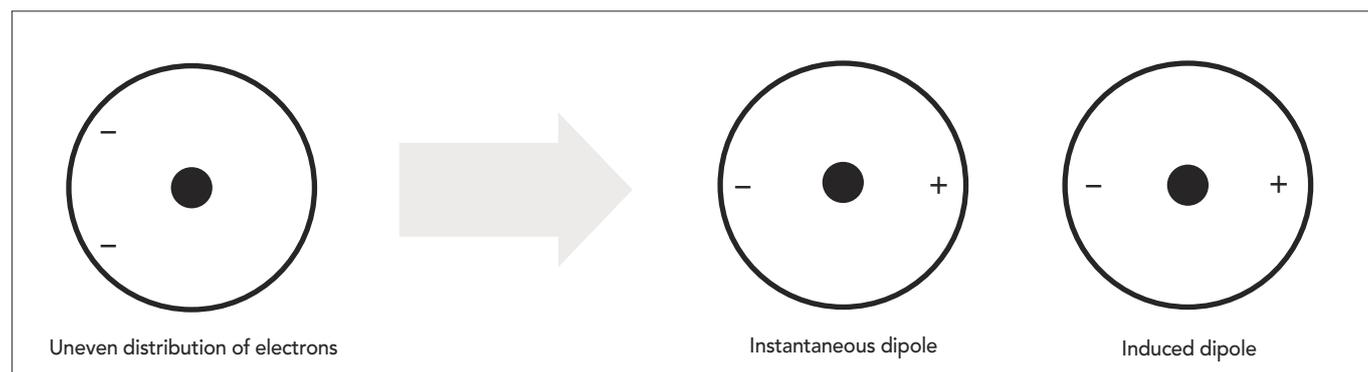


Figure 2: A representation of London dispersion forces.⁵

London dispersion forces are the attraction between molecules due to instantaneous areas of charge as a result of localised electron movement.

Figure 2 shows how the uneven distribution of electrons at any moment due to random electron movement results in a dipole that, albeit short lived, induces a dipole in a neighbouring molecule, resulting in a small attractive force.

Individually, these forces are very weak compared to hydrogen bonds or covalent bonds, but as molecules start to get bigger, the degree of interaction increases and the sum of the forces starts to become significant. This effect causes the increase in boiling points of esters as their molecular weights increase, seen in Table 1.^{6,7}

As the molecular weight of the materials increases, so does the boiling point. This is almost entirely due to the increased attraction between molecules as a result of London dispersion forces. This increase of intermolecular attraction is also felt in the sensory properties of the material. As the attraction between the molecules increases, more force has to be applied in order for the layers of molecules to slide against each other, leading to lower spreadability and a heavier feel. This effect can be felt when comparing two similar molecules such as Isononyl Isononanoate (18 carbons) and Isotridecyl Isononanoate (22 carbons). They have very similar structures and only differ by 4 carbons, but even with this small change, a slight difference can already be felt. This effect will be more apparent when the difference in molecular weights becomes larger.

The effect of branching

It has been established that a larger molecular weight results in a greater degree of London dispersion interaction and so a heavier skin-feel. This holds true for linear molecules but this rule breaks down when taking branching into account. When considering London dispersion forces, it is essential to take into account how well the molecules 'stack' in layers. The better they 'stack' the more effective the interaction and heavier the skin-feel. Branching disrupts how effectively the molecules can stack and hence disrupts this key interaction. This reduces the amount of interaction between the molecules and results in a lower boiling point and a lighter skin-feel.

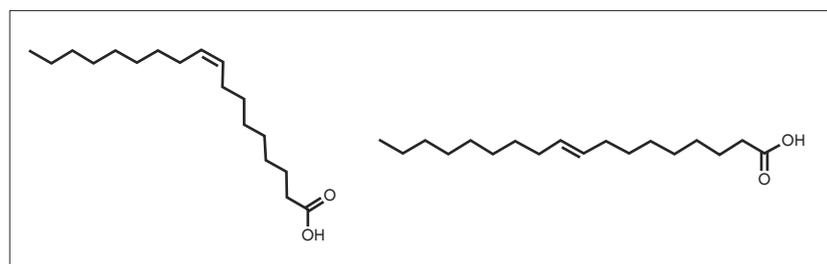


Figure 3: The structures of the oleic acid (left) and its trans isomer, elaidic acid.

Ester Name	Ester Structure	Molecular Weight	Boiling Point/°C
Ethyl Formate		74.1	54
Ethyl Acetate		88.1	77
Ethyl Hexanoate		144.2	168
Ethyl Decanoate		200.3	244
Ethyl Dodecanoate		228.4	269

Table 1: The relationship between the molecular weight of different esters and their relative boiling points.⁷

The effect of unsaturation

Only saturated molecules (molecules with no double bonds) have been considered thus far. The degree of unsaturation also has an effect on the skin-feel of esters. Each bond in a saturated compound has 360° free rotation, allowing the material to be extremely flexible and conform to the most energetically favourable state, i.e. favouring high London dispersion interactions. Double bonds do not have this free rotation and fix the molecule in a certain conformation. This makes them less flexible and leads to a reduction in the strength of London dispersion forces and a lighter skin-feel. This can be seen by comparing the melting point of Isopropyl Stearate (30°C) and Isopropyl Oleate (-15°C).⁸

This effect is more pronounced when comparing cis and trans conformations. The cis conformation disrupts the structure far more and results in a lower melting point and therefore a lighter skin-feel. This is seen with many types of unsaturated molecules and is demonstrated by comparing the melting points of Oleic Acid (13°C) with its trans isomer Elaidic Acid (43°C). This is made more significant by the fact that in natural triglycerides, unsaturation that occurs is predominantly in the cis conformation.^{8,9,10}

Polyol-derived esters

Some esters are formed using a polyol as a

starting material. A polyol is a molecule with multiple alcohol functional groups. Some common examples include tricapylin, which is derived from glycerin, a tri-ol, and esters derived from pentaerythritol, a tetra-ol. Esters derived from polyols are inherently more branched than ones derived from mono alcohols, and so even though they can be quite large molecules, they feel quite light on the skin. The complex structures of polyols give a unique skin-feel. Pentaerythrityl esters, for example (Fig 4), give a more cushioned sensation on the skin so are good materials to use when aiming to achieve a soft skin-feel.^{7,11}

Hydrogen bonding and hydroxyl groups

Hydroxyl groups are a fairly common functional group in ester compounds and are easily identifiable from the INCI name, such as Ethylhexyl Hydroxystearate. These groups tend to make the material feel heavier and more moisturising. This is another example of the wide range of sensory properties that can be achieved with esters.¹²

Cascade effect

These factors all affect how the ester, and ultimately the final product, will feel on the skin. Depending on the desired application different esters should be used. For a light, fast drying application, short chain or

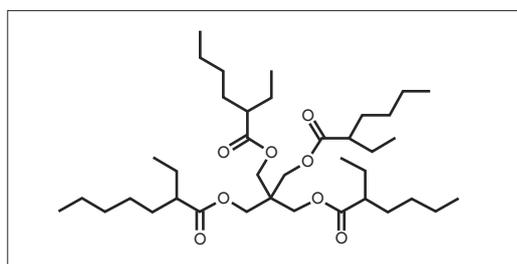


Figure 4: The structure of pentaerythrityl tetraethylhexanoate.

branched esters would be suitable; a heavier, alcohol-modified ester may be more suited to a more substantive product such as a moisturiser. Normally a single emollient in the oil phase does not achieve an elegant texture as the sensory properties can become slightly one dimensional. Emollients that are too heavy leave the skin feeling moisturised but are unpleasant on application, whereas light emollients can result in an overly dry skin-feel. The 'Cascading Emollients' theory promotes the idea that through the combination of three or more emollients, a huge variety of pleasant textures can be achieved throughout all stages of product use; initial application, rub-in and after-feel.^{13,14}

Functional properties of ester emollients

Compatibility with organic UV filters

Esters are becoming prevalent in many application areas and especially in sun care. The primary reason for this is that esters are extremely compatible with organic UV filters. This is because organic UV filters tend to be polar and some, like Octyl Salicylate and Octyl Methoxycinnamate, are in fact esters. This means that organic UV filters are highly soluble in esters, much more so than in more traditional oils or silicones. Cost-savings can therefore be achieved by using esters, as lower levels of esters can be used to achieve complete solubilisation of the UV filter. Complete solubilisation and even distribution of the UV filter in the final product is essential for achieving high and consistent SPF levels.^{15,16}

The generally dry skin-feel of esters can be used to counteract the unpleasant

aesthetics of certain filters, which can be noticeably tacky or greasy. This is especially true of Octocrylene, which is being used increasingly often due to its compatibility with Avobenzone versus the reported instabilities between Ethylhexyl Methoxycinnamate and Avobenzone. However Octocrylene is often considered to have an unpleasant, sticky feel, which can be minimised by being formulated in combination with light esters. Optimal design of sun care formulations to ensure that they have pleasant aesthetics as well as being photo-stable and with high SPF is important in encouraging consumers to apply sufficient doses of sun care products.

Pigment wetting in colour cosmetics

Esters are commonly used liquids in aiding the pigment wetting process. Pigment wetting is the first step in the dispersion process, where the air that surrounds the solid pigment particles is substituted by a liquid. This is essential in order to achieve consistently high colour intensity. For the liquid to wet the solid pigment, the surface tension of the liquid must be lower than that of the solid. Other materials are often added to the liquid to reduce its surface tension and hence wet the pigment more effectively. Esters tend to have lower surface tension than other oils and so are very effective pigment wetting agents, and can also achieve pigment wetting with lower levels of additives than other oils.

A lower surface tension not only results in easier pigment wetting but also leads to improved spreadability. This is another desirable property in colour cosmetic applications, as a product that spreads well tends to be easier and more comfortable to apply.¹⁷

Ester stability

Esters are relatively simple to manufacture, via a small number of chemical reactions. The breakdown of esters back into their constituent parts is also straightforward, and this has to be taken into account when formulating with esters.

Acidic and basic conditions can lead to the hydrolysis of esters, resulting in their breakdown into an alcohol and a carboxylic acid. This begins to become an issue at a pH lower than 5 or higher than 10. The rate of the hydrolysis reaction is directly related to the pH, with the ester being hydrolysed more quickly as the pH extends further from the advised pH range. This is a limitation for the use of esters as many personal care applications require either a high or a low pH. For example certain hair treatments and depilatory products have a very high pH, while AHA products and chemical exfoliants require a low pH.

The rate of hydrolysis is not only affected by the pH but also by the structure of the ester itself. When considering the hydrolytic stability of esters there are two main structural factors to consider: the electronic and steric properties of the molecule.

In terms of electronic properties, the main consideration is the polarity of the ester. A higher polarity makes materials more hydrophilic, and so more water soluble. In general, this leads to lower hydrolytic stability as interaction between water and the ester linkage is fundamental to the reaction. Longer carbon chains on the ester can reduce the polarity of the molecule and thus reduce its susceptibility to hydrolysis, whereas functionalities such as hydroxyl groups increase polarity and so

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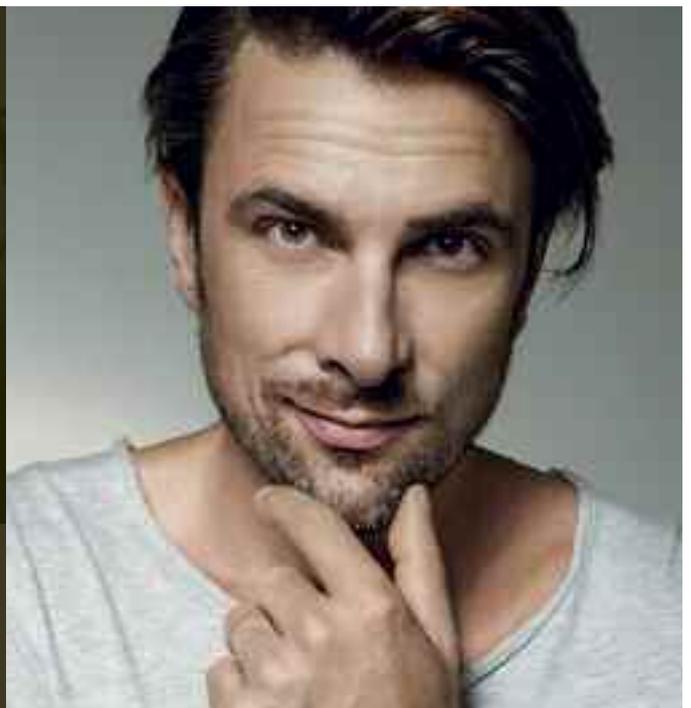
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facilitate the hydrolytic reaction.

In terms of steric properties, it is important to consider the accessibility of water to the reaction site, in this case the ester group. Esters that have a highly branched structure are more hydrolytically stable as this branching acts as a physical barrier that blocks some degree of the water's access to the reaction site. If the hydrolytic stability of esters in formulations is a concern, it is advised to either choose one with a low polarity or one that is highly branched as these factors can significantly reduce the rate at which esters are hydrolysed.

Conclusion

Esters have been increasingly used in cosmetic formulations over the past few years. Esters are currently used in a wide variety of applications for their sensorial and emollient properties. Esters also have the potential to provide functional alternatives to silicones, for formulators who wish to avoid cyclic silicones or silicones in general. Esters can be synthesised from natural precursors, which represents a great opportunity for esters to thrive in the industry as trends continue towards more natural and naturally-derived products. While selecting the best ester for a particular formulation may at first appear to be difficult, in fact the functional, sensory and stability properties of esters all relate to their chemical structures. Consequently, formulators who understand how the structure of an ester affects its characteristics can select the optimum ester for their application quickly and reliably. PC

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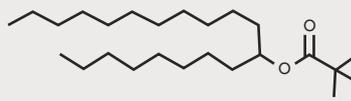
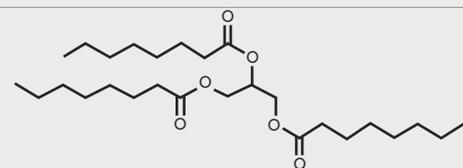
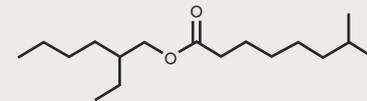
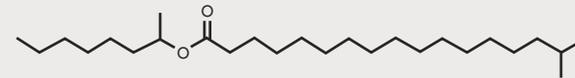
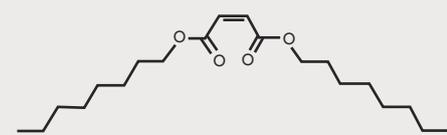
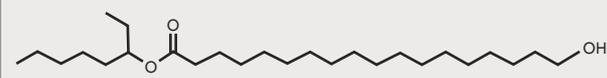
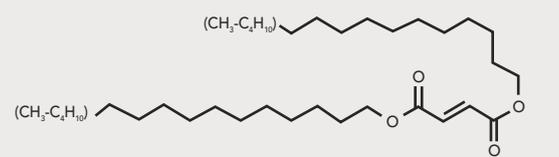
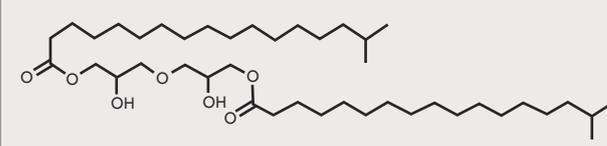
INCI name and Properties	Chemical Structure
Octyldodecyl Neopentanoate Skin Feel: Very light Dielectric Constant: 3.02	
Tricaprylin Skin Feel: Very light Dielectric Constant: 3.89	
Ethylhexyl Isononanoate Skin Feel: Light Dielectric Constant: 3.39	
Methylheptyl Isostearate Skin Feel: Light Dielectric Constant: 3.14	
Dicaprylyl Maleate Skin Feel: Light Dielectric Constant: 4.62	
Ethylhexyl Hydroxystearate Skin Feel: Medium Dielectric Constant: 3.92	
Di-C12-15 Alkyl Fumarate Skin Feel: Solid / Medium Dielectric Constant: –	
Polyglyceryl-2 Diisostearate Skin Feel: Heavy Dielectric Constant: 4.26	

Table 2: Interesting esters with their structure and properties.

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